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Iron(0)tricarbonyl Complexes of Microbially-Derived Cyclohexadiene Ligands Containing Quaternary Stereocenters

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Fe(CO)₃ Cyclohexadienes with Quat. Stereocenters.

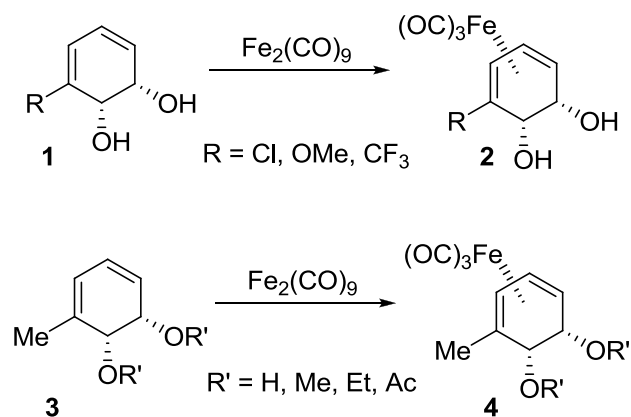
[†]University of Bath.

[‡]Prosidion Limited.

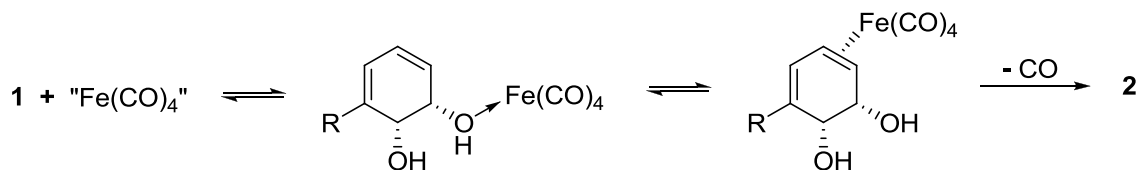
Summary: Tricarbonyliron(0) complexes of novel cyclohexadiene ligands possessing quaternary centers have been synthesized and characterized by ¹H and ¹³C NMR and by X-ray crystallography. The ligands, which are derived via an unusual microbial oxidation of benzoic acid, have been shown to undergo oxidative modification post-complexation. The factors that influence facial discrimination upon complexation are discussed.

Introduction

The first example of a tricarbonyl(cyclohexadiene)iron complex was reported by Pauson over 50 years ago.¹ Such complexes have since proven to be of great utility as intermediates in synthesis due to the stereocontrol that may be exerted in diene coordination and subsequent ligand manipulation.² Synthesis of enantiopure tricarbonyl(diene)iron complexes requires either coordination of the tricarbonyliron fragment with a prochiral diene and a subsequent resolution of enantiomers, use of an asymmetric tricarbonyliron transfer agent³ or, more directly, diastereoselective coordination of the tricarbonyliron fragment with a diene ligand already containing one or more stereocenters. The resultant facial isomers in this case are diastereoisomeric, hence are separable without recourse to resolution; indeed, if transfer of stereochemical information from the preexisting stereocenter(s) is efficient, a single isomer may be produced. Rigid cyclohexadiene ligands where one or both of the sp^3 -hybridized carbons are stereocenters exhibit excellent stereinduction upon complexation, when Lewis-basic substituents are present, as shown by the examples from Stephenson⁴ and Pearson⁵ illustrated in Scheme 1. The complete stereoselectivity in complexation observed has been rationalized in terms of precoordination of a 16 valence-electron tetracarbonyliron fragment to one of the ligand hydroxy groups (Scheme 2).

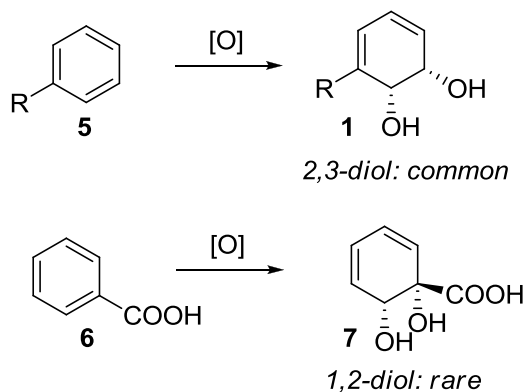


Scheme 1. Single (*endo*) isomer obtained in each instance



Scheme 2.

The cyclohexadiene diols **1** are available in enantiopure form via the microbially-mediated dearomatizing oxidation of arene precursors. In excess of 400 such arene-derived diols are known and have found extensive applications in synthesis.⁶ In the vast majority of cases, substituted arenes are metabolized to furnish 2,3-diols of type **1**. Much rarer are examples that furnish 1,2-diols such as **7** (Scheme 3).

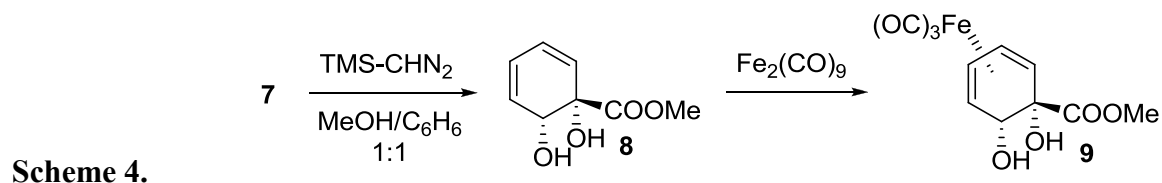


Scheme 3.

The conversion of benzoic acid to 1,2-dihydroxycyclohexa-3,5-diene-1-carboxylic acid (**7**, >95% *e.e.*) can be effected by *R. eutrophus* B9⁷ and Myers has recently demonstrated the versatility of this compound as a building block for organic synthesis.⁸ However, to date it has not been used in organometallic chemistry. The 1,2-diol **7** differs from the 2,3-diols used by Pearson and Stephenson in that one of the *sp*³ carbons is a quaternary center. We report below that this difference is relevant in the contexts of facial selectivity upon complexation and of subsequent derivatization of the ligand. Numerous examples of tricarbonyl(cyclohexadiene)iron complexes possessing a quaternary center on the cyclohexadiene ligand are known. However, the majority of these are assembled by ligand modification post-complexation,⁹ often by a $[\eta^4] \rightarrow [\eta^5]^+ \rightarrow [\eta^4]$ sequence.¹⁰ Complexation of a tricarbonyliron fragment to a cyclohexadiene ligand with a preexisting quaternary center is much less common.¹¹ So far, the only *enantiopure* ligands incorporating this structural motif that have been used for tricarbonyliron complex formation have been polycyclic steroid derivatives.¹² Thus, to our knowledge, this work constitutes the first report of tricarbonyliron complex formation from an enantiopure non-annelated cyclohexadiene possessing a quaternary center.

Results and Discussion

We first attempted the direct complexation of **7** by treatment with $\text{Fe}_2(\text{CO})_9$ in THF, but this resulted only in intractable mixtures. We therefore derivatized **7** as the corresponding methyl ester **8** by treatment with trimethylsilyldiazomethane in methanol/benzene.^{8c} The resultant crude ester was then directly treated with $\text{Fe}_2(\text{CO})_9$ to furnish *endo* complex **9** as the sole isomer (Scheme 4).



Optimization of reaction conditions established that THF afforded marginally superior yields to Et_2O . The thermal instability of **8** precluded heating (it decomposes above room temperature via a facile elimination of water with concomitant rearomatization), but a long reaction time (16 d) could be simply employed instead, giving **9** in 55% yield (over 2 steps) as a yellow air-stable solid after purification by chromatography. Single crystals of complex **9** suitable for X-ray structure determination were obtained from diffusion of petroleum ether into a solution of **9** in CH_2Cl_2 (Figure 1).

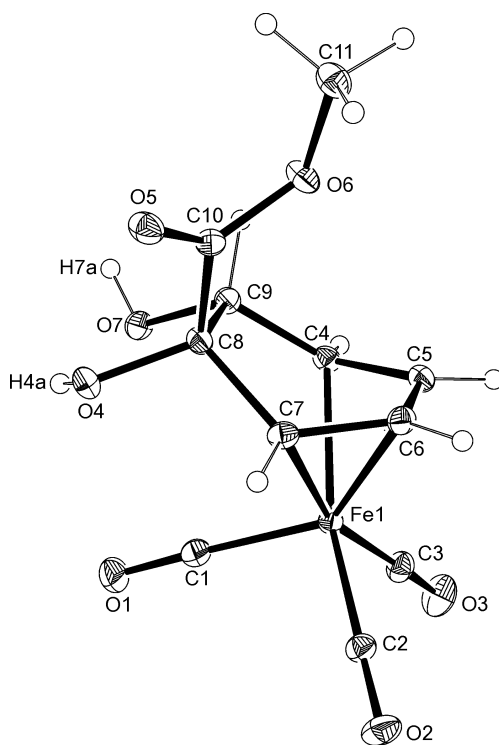


Figure 1. Solid state structure of **9**. Ellipsoids are represented at 30% probability.

In the initial formation of complex **9**, we considered it to be significant that a single facial isomer was produced. As discussed above, there is extensive precedent for stereocontrol when Lewis-basic hydroxyl or ether group(s) are present. However, ester groups are also reported to exert control over stereoselectivity of facial complexation.¹³ As such, due to the quaternary center in **8**, it may be regarded as a “competition ligand”, in that both diene faces present Lewis-basic functionality towards an incipient tetracarbonyliron fragment. One other such example, from Berchtold and Ashworth, exists in the literature,¹⁴ in which the cyclohexadiene ligand possesses an acetate group on one face and, on the adjacent carbon, a methoxy group on the other face. In this case, the sole isomer formed upon complexation is that in which the acetate group is *endo*, (\pm)-**10**, implying that the acetate functionality is a markedly better site of coordination for the incoming tetracarbonyliron fragment than the methyl ether. In contrast, our example shows a diol to be a markedly more effective directing group than a methyl ester (Figure 2).

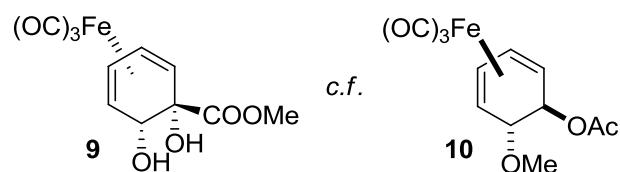
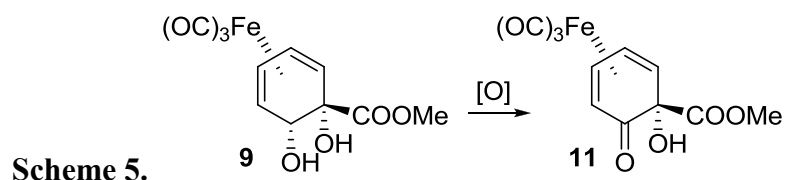


Figure 2. Berchtold’s precedent for complexation of “competition” ligands.

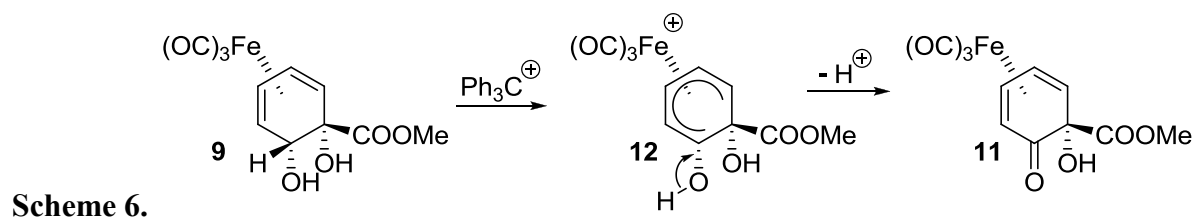
This complete reversal of effects (ester dominant directing group *vs.* ester not dominant directing group) may plausibly be rationalized not only in terms of the superior directing ability of the diol, but also in terms of ester regiochemistry – in complex (\pm)-**10** the ester carbonyl oxygen (presumed initial site of coordination) is more remote than in complex **9**.

With diol **9** in hand, we sought to modify the diene ligand to access complexes that would not be accessible from the corresponding uncomplexed diene. Specifically, we undertook the oxidation of the secondary alcohol in **9** to form cyclohexadienone complex **11** (Scheme 5). The corresponding free cyclohexadienone ligand is not known and a close analogue (derivatized at the tertiary alcohol) has been

shown to be unstable with respect to Diels–Alder dimerization,^{8c} as is the case for many cyclohexadienones.



We anticipated that the transformation depicted in Scheme 5 would be challenging, since it constitutes a selective oxidation of the alcohol in the presence of the oxidatively labile tricarbonyliron moiety. An approach which has been shown to be compatible with tricarbonyliron(diene) complexes is hydride abstraction with trityl salts proceeding via a η^5 intermediate (Scheme 6). Treatment of complex **9** with trityl tetrafluoroborate in CH_2Cl_2 did indeed provide access to **11** as a slightly air sensitive yellow solid, but in low yield (26% after chromatography), which could not be improved upon variation of the reaction conditions. In considering possible reasons for this low yield, consideration was given to *dehydroxylation* as opposed to hydride abstraction as an alternative reaction manifold (the η^5 product of dehydroxylation would not be expected to be stable¹⁴). Such competing pathways have been observed previously.^{4b,c} Electron-withdrawing groups have been shown to favor hydride abstraction over dehydroxylation, but this has been demonstrated conclusively only when the EWG is in conjugation with the diene;⁵ the likely electronic influence of the ester in **9** on the reaction pathway may therefore not be predicted with confidence. Moreover, both hydride abstraction and dehydroxylation with trityl salts are very sensitive to steric hindrance.¹⁵ Thus, dehydroxylation is not plausible in this instance as it would require approach of the bulky trityl cation to the *endo* face. Similarly, the presence of the *exo* ester functionality on the quaternary center in **9** likely retards the approach of the bulky trityl cation to the adjacent *exo* hydride.



We undertook to improve the yield of **11** by screening different oxidations.¹⁶ Manganese dioxide transpired to be the only oxidant able to furnish **11** in a useful yield (59%). The success of MnO₂ in effecting this transformation is particularly noteworthy, since whilst it is an oxidant of choice for oxidation of *uncomplexed* allyl alcohols, to date it has not been reported for the corresponding transformation of tricarbonyliron(cyclohexadienol) complexes. Three examples have been reported for tricarbonyliron complexes of other dienol ligand types (cyclobutadiene¹⁷ and acyclic dienes¹⁸), but far more prevalent in the literature are examples of manganese dioxide effecting oxidative cleavage of the tricarbonyliron fragment from the diene.¹⁹ Also, a preference for transfer of an *endo* hydride to the oxidant has been noted²⁰ in manganese dioxide-induced cyclizations of tricarbonyliron(diene) complexes, in contrast to the example at hand, which necessarily involves *exo* hydride removal.

Single crystals of complex **11** suitable for X-ray structure determination were obtained from diffusion of petroleum ether into a solution of **11** in CH₂Cl₂ (Figure 3).

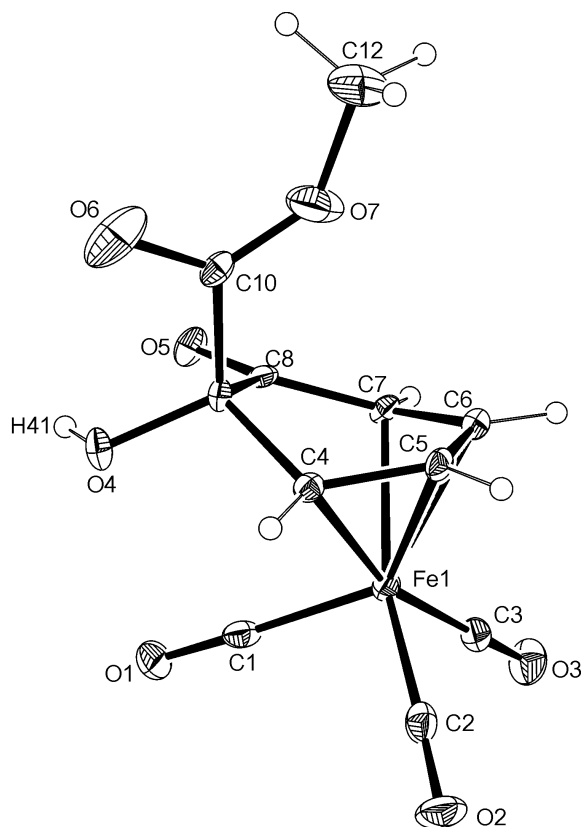


Figure 3. Solid state structure of one of the six ketone molecules in the asymmetric unit of **11**. Ellipsoids are represented at 30% probability. Disordered partial atoms omitted for clarity.

It is revealing to compare the NMR spectra of complexes **9** and **11**. For complex **9**, all ^1H and ^{13}C resonances were assigned unambiguously by means of COSY, HMQC and HMBC spectra. The presence of the ester in **9** perturbs the chemical shifts of the diene protons such that the internal diene protons H4 and H5 resonate at 5.39 and 5.34 ppm respectively ($\Delta\delta = 0.05$ ppm). The corresponding protons in the complex lacking the ester (**2**, R=H) are observed at 5.29 ppm.²¹ The external diene protons in complex **9** display a more pronounced separation, with H3 and H6 observed at 3.21 and 2.84 ppm respectively ($\Delta\delta = 0.37$ ppm).²² In the ^{13}C spectrum, the iron carbonyls are observed as a single resonance at 210.2 ppm, indicative of fast turnstile rotation of these ligands at room temperature. In contrast to diol complex **9**, all ^1H and ^{13}C resonances of ketone complex **11** could not be assigned unambiguously. Specifically, the pair of external diene signals (H3 and H6) could not be differentiated, nor could the pair of internal diene signals (H4 and H5); 2D NMR experiments did not resolve this ambiguity and a possible nOe interaction between the methyl ester protons and H6 was not observed. Regardless, it is interesting to compare the observed chemical shifts with those for complex **9**. The effect of additional electronic perturbation due to the ketone is such that for complex **11**, the separation of the internal diene protons H4 and H5 ($\Delta\delta = 0.27$ ppm) is greater than that for the external diene protons H3 and H6 ($\Delta\delta = 0.08$ ppm), the opposite effect to that observed for **9**. In the ^{13}C spectrum of **11**, the iron carbonyls are again observed as a single resonance, but at a lower chemical shift (207.3 ppm) than for those in **9**. We ascribe this upfield shift to the enhanced π -acidity of the dienone ligand²³ in **11** with respect to the diene in **9**, and the corresponding decrease in back-bonding to the carbonyl ligands. Additional evidence for this may be seen in the infrared spectra (ν_{CO} 2069, 1991 cm^{-1} for **11**, ν_{CO} 2049, 1958 cm^{-1} for **9**). The X-ray structural determinations reveal a mean Fe–C bond length of 1.798 Å for the carbonyl ligands in **9**, which is comparable to those observed for the two other reported tricarbonyliron(cyclohexadienediol) X-ray structures (**2**, R=CF₃, with a mean Fe–C bond length of 1.794 Å for the carbonyl ligands⁵ and the bis(benzoate) of **2**, R=H, with a mean Fe–C bond length of 1.800 Å for the carbonyl ligands²¹). In striking contrast, the mean Fe–C bond length for the carbonyl ligands in **11** is 1.814 Å, also highly suggestive of decreased iron-to-carbonyl back-bonding in this complex.

In conclusion, we have introduced a novel class of ligand for tricarbonyliron chemistry and demonstrated the viability of post-complexation ligand modification. The complexes reported herein afford some insight into the relative magnitude of the directing effects of various functional groups in tricarbonyliron complexation.

Experimental Section

General Procedures and Instrumentation. Reactions which required the use of anhydrous, inert atmosphere techniques were carried out under an atmosphere of nitrogen. Nonacarbonyldiiron was dispensed in a glovebox, but all subsequent isolation and purification procedures were performed in a fumehood, open to the atmosphere. Solvents were dried and degassed by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. Petrol refers to petroleum ether, bp 40-60 °C. TLCs were performed using aluminum-backed plates precoated with Alugram[®]SIL G/UV and visualized by UV light (254 nm) and/or KMnO₄ followed by gentle warming. Flash column chromatography was carried out using Davisil LC 60Å silica gel (35-70 micron) purchased from Fisher Scientifics. Nonacarbonyldiiron was purchased from Sigma-Aldrich and used as received. IR spectra were recorded on Perkin-Elmer 1600 FT IR spectrometer with absorbances quoted as ν in cm⁻¹. NMR spectra were run in CDCl₃ on Brüker Avance 300 or 500 MHz instruments at 298 K. Mass spectra were recorded with a microTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Brüker Daltonik). Specific rotations were recorded on an Optical Activity AA-10 Automatic polarimeter with a path length of 1 dm. Concentrations (c) are quoted in g/100 mL. Elemental analyses were performed using an Exeter Analytical CE 440 analyzer.

Synthesis of (–)-(3*S*)-Tricarbonyl(η^4 -(1*S*,2*S*)-methyl 1,2-dihydroxycyclohexa-3,5-dienecarboxylate)iron(0) (9). To 1.11 g (7.09 mmol, 1.00 equiv) of **7** was added benzene-MeOH (1:1, 100 mL). The resultant turbid solution was stirred at room temperature and Trimethylsilyldiazomethane (2.0M solution in hexanes) was added dropwise via syringe over 15 mins until effervescence ceased and a yellow color persisted (\approx 6.5 mL). The reaction mixture was stirred for 2 h, then concentrated under

reduced pressure and dried under high vacuum to give crude ester **8**, (1.21 g, 100%), used immediately without purification. To this crude ester **8** was added nonacarbonyldiiron (2.79 g, 7.67 mmol, 1.08 equiv). THF (100 mL) was added and the reaction mixture was stirred at room temperature for 7 d. An aliquot was removed and analyzed by NMR, which indicated the presence of unreacted **8**. Thus, the reaction mixture was added via cannula to an additional portion of nonacarbonyldiiron (2.73 g, 7.49 mmol, 1.05 equiv) and stirred at room temperature for 9 d. The reaction mixture was concentrated under reduced pressure (*Care! Toxic pentacarbonyliron distilled over at this point*) and the crude product was purified by chromatography (40% EtOAc-petrol) to give **9** (1.37 g, 55% over 2 steps) as a yellow solid. Crystals suitable for X-ray diffraction were grown from CH₂Cl₂/petroleum at room temperature; mp 130-132 °C; *R_f* 0.22 (40% EtOAc-petrol); *R_f* 0.74 (70% EtOAc-petrol); [α]_D²⁵ -190° (c 0.1, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃): δ 5.39 (1H, dddd, *J* = 6.0, 4.0, 1.5, 1.0 Hz, H4), 5.35 (1H, ddd, *J* = 6.0, 4.5, 2.0 Hz, H5), 3.91-3.88 (1H, m, H2), 3.88 (1H, s, C1-OH), 3.74 (3H, s, -OCH₃), 3.21 (1H, dt, *J* = 6.5, 2.0 Hz, H3), 3.17 (1H, d, *J* = 7.0 Hz, C2-OH) 2.84 (1H, dd, *J* = 6.0, 2.0 Hz, H6); ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 210.2 (3 \times Fe(CO)), 174.9 (-COOCH₃), 84.6 (C5), 84.3 (C4), 77.3 (C1), 72.1 (C2), 67.4 (C3), 64.5 (C6), 53.5 (-COOCH₃); ν_{max} (film) 3417, 3007, 2957, 2049 (Fe ν_{CO}), 1958 (Fe ν_{CO}), 1723 (ester ν_{CO}), 1436, 1381, 1236, 1172, 1135, 1062, 1020, 981, 940, 911, 869, 831, 794, 732 cm⁻¹; ESI-TOF MS: [M + Na]⁺ *m/z* = 332.9657 (theoretical *m/z* = 332.9674). Anal. Calcd for C₁₁H₁₀FeO₇: C, 42.6; H, 3.25. Found: C, 43.0; H, 3.22.

Synthesis of (–)-(3*S*)-Tricarbonyl(η^4 -(1*S*)-methyl 1-hydroxy-2-oxocyclohexa-3,5-dienecarboxylate)iron(0) (11**).** To diol **9** (983 mg, 3.17 mmol, 1.00 equiv), activated powdered 4Å molecular sieves (280 mg) and MnO₂ (5.51 g, 63.4 mmol, 20.0 equiv) was added CH₂Cl₂ (50 mL). The reaction mixture was stirred at room temperature for 21 h, then filtered through a plug of Celite, washed through with CH₂Cl₂. The filtrate was concentrated under reduced pressure and purified by chromatography (8% isopropanol-hexane) to give **11** as a yellow powder (572 mg, 59%). Crystals suitable for X-ray diffraction were grown from CH₂Cl₂/petroleum at room temperature; mp 122 °C; *R_f* 0.13 (8% isopropanol-hexane); [α]_D²⁵ -160° (c 0.1, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃): δ 5.92 (1H,

ddd, $J = 6.0, 5.0, 2.0$ Hz, H4 or H5), 5.65 (1H, ddd, $J = 6.5, 5.0, 1.5$ Hz, H4 or H5), 4.05 (1H, s, -OH), 3.70 (3H, s, -OCH₃), 3.42 (1H, dd, $J = 6.0, 1.0$ Hz, H3 or H6), 3.34 (1H, dd, $J = 6.5, 2.0$ Hz, H3 or H6); ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 207.3 (3 \times Fe(CO)), 188.8 (C2), 170.3 (-COOCH₃), 86.6 (C4 or C5), 84.7 (C4 or C5), 73.1 (C1), 60.7 (C3 or C6), 56.9 (C3 or C6), 53.3 (-CH₃); ν_{\max} (film) 3430, 2957, 2917, 2850, 2069 (Fe ν_{CO}), 1991 (Fe ν_{CO}), 1737 (ester ν_{CO}), 1667 (ketone ν_{CO}), 1455, 1364, 1254, 1224, 1130, 1100, 1025, 978, 801, 733 cm⁻¹; ESI-TOF MS: $[M + H]^+ m/z = 308.9702$ (theoretical $m/z = 308.9697$). Anal. Calcd for C₁₁H₈FeO₇: C, 42.9; H, 2.62. Found: C, 43.0; H, 2.60.

X-ray Structure Determination. Single crystals of compounds **9** and **11** were analysed at 150 K, using Mo($K\alpha$) radiation on a Nonius Kappa CCD diffractometer. Details of the data collections, solutions and refinements are given in Table 1. The structures were solved using SHELXS-97²⁴ and refined using full-matrix least squares in SHELXL-97²⁴. Data collection, structure solution and refinement of the model posed no problems for compound **9**. However, the meandering route towards the presented model for **11** was not straightforward. In the first instance, obtaining crystals of suitable quality involved copious strenuous efforts. This became increasingly important after the first of eight data collections suggested that the crystal structure would only solve in space group *P1* with six molecules in the unit cell. The mediocre quality of the first crystal batch plus the concern that the sample might be twinned (the unit cell can be metrically transformed into a monoclinic *C* setting) necessitated very rigorous analysis before presenting the data herein. Thus, some months later, several data sets and extensive study has afforded a model that arises from a small, but non-twinned crystal, for which one can be confident the space group is correct – this crystallographer having previously doubted this symmetry possibility. Once an optimum data set had been obtained for **11**, as described above, refinements were generally straightforward with the following exceptions and points of note. Firstly, in **11**, the methoxy groups in all six ester moieties are disordered in a 50:50 ratio with the carbonyl functionality present in the same ester. Hydrogen atoms attached to the diene carbons were located in both structures, and refined at a distance of 0.98 Å from the relevant parent atoms. The absolute configuration could be readily determined via the X-ray data. Intermolecular hydrogen bonding

involving the hydroxyl proton of the functionality attached to the quaternary carbon, and the oxygen (hydroxyl in **9**, ketonic in **11**) bonded to the neighboring carbon in the cyclohexadiene moiety was clearly evident. In addition, H7a in **9**, interacts with O5 from a proximate lattice neighbor to render hydrogen-bonded chains along the *b* axis in the gross structure.

Acknowledgements. We thank Prosidion Limited, EPSRC and CIKTN for a CASE studentship (to MAK) and the University of Bath for additional funding. We thank Prof. Andrew G. Myers (Harvard) for a generous gift of *R. eutrophus* B9 cells. We also thank Dr G. Richard Stephenson (UEA), Dr Andrew L. Johnson (Bath) and Dr Michael K. Whittlesey (Bath) for helpful discussions and Dr Petra J. Cameron (Bath) for translation.

Supporting Information Available: A CIF file giving crystal data for compounds **9** and **11**. This material is available free of charge via the internet at <http://pubs.acs.org>. These crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 750836 – 750837. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

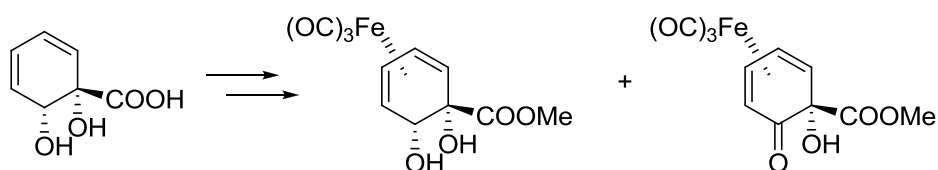
Table 1. Crystal data and structure refinement for compounds **9** and **11**.

Compound	9	11
Empirical formula	C ₁₁ H ₁₀ FeO ₇	C ₁₁ H ₈ FeO ₇
Formula weight	310.04	308.02
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 1
<i>a</i> / Å	8.0220(1)	6.6880(3)
<i>b</i> / Å	8.1780(1)	6.7010(3)
<i>c</i> / Å	18.1270(3)	46.634(2)
α / °	90	85.896(1)
β / °	90	85.972(2)
γ / °	90	60.254(3)
<i>U</i> / Å ³	1189.20(3)	1808.47(15)
<i>Z</i>	4	6
<i>D_c</i> / gcm ⁻³	1.732	1.697
μ / mm ⁻¹	1.295	1.277
<i>F</i> (000)	632	936
Crystal size / mm	0.20 x 0.30 x 0.40	0.22 x 0.07 x 0.07
Theta min., max for data collection	3.56, 29.13	4.21, 25.00
Index ranges	-10 ≤ <i>h</i> ≤ 10; -11 ≤ <i>k</i> ≤ 11; -24 ≤ <i>l</i> ≤ 24	-7 ≤ <i>h</i> ≤ 7; -7 ≤ <i>k</i> ≤ 7; -55 ≤ <i>l</i> ≤ 55
Reflections collected	25065	14425
Independent reflections, <i>R</i> _{int}	3187, 0.0524	9757, 0.0357
Reflections observed (>2σ)	2889	8640
Absorption correction	Multi-scan	Multi-scan
Max., min. transmission	0.68, 0.63	0.787, 0.745
Data / restraints / parameters	3187 / 4 / 193	9757 / 27 / 1177
Goodness-of-fit on <i>F</i> ²	1.108	1.023
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0259, 0.0588	0.0318, 0.0629
Final <i>R</i> 1, <i>wR</i> 2 (all data)	0.0349, 0.0622	0.0418, 0.0662
Absolute structure parameter	-0.034(14)	-0.017(10)
Largest diff. peak, hole / eÅ ⁻³	0.644, -0.856	0.330, -0.362

Iron(0)tricarbonyl Complexes of Microbially-Derived Cyclohexadiene Ligands Containing Quaternary Stereocenters

Monika Ali Khan, Mary F. Mahon, Alan J. W. Stewart and Simon E. Lewis*

Tricarbonyliron(0) complexes of novel, microbially-derived, cyclohexadiene ligands possessing quaternary centers have been synthesized and characterized by X-ray crystallography and by ^1H and ^{13}C NMR. Ligand oxidation post-complexation has been demonstrated and the factors that influence facial discrimination upon complexation are discussed.



¹ Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1958**, 642.

² (a) Bauer, I.; Knölker, H.-J. Iron complexes in organic chemistry. In *Iron Catalysis in Organic Chemistry*; Plietker, B., Ed.; Wiley-VCH: Weinheim, Germany, 2008; pp 1–27. (b) Stephenson, G. R. *Science of Synthesis* **2002**, 1, 778. (c) Knölker, H.-J.; Braier, A.; Bröcher, D. J.; Cämmerer, S.; Fröhner, W.; Gonser, P.; Hermann, H.; Herzberg, D.; Reddy, K. R.; Rohde, G. *Pure Appl. Chem.* **2001**, 73, 1075. (d) Donaldson, W. A. *Curr. Org. Chem.* **2000**, 4, 837. (e) Iwata, C.; Takemoto, Y. *Chem. Commun.* **1996**, 2497. (f) Grée, R.; Lellouche, J. P. Acyclic Diene Tricarbonyliron Complexes in Organic Synthesis. In *Advances in Metal-Organic Chemistry*; Liebskind, L. S., Ed.; JAI Press: Greenwich, CT, USA, 1995, pp 129–273. (g) Pearson, A. J. *Synlett* **1990**, 10. (h) Stephenson, G. R.; Alexander, R. P.; Morley, C.; Howard, P. W. *Phil. Trans. R. Soc. Lond. A* **1988**, 326, 545.

³ (a) Knölker, H.-J.; Hermann, H. *Angew. Chem., Int. Ed.* **1996**, 35, 341. (b) Knölker, H.-J.; Goesmann, H.; Hermann, H.; Herzberg, D.; Rohde, G. *Synlett* **1999**, 421. (c) Knölker, H.-J. *Chem. Rev.* **2000**, 100, 2941.

⁴ (a) Stephenson, G. R.; Howard, P. W.; Taylor, S. C. *J. Organomet. Chem.* **1991**, 419, C14. (b) Howard, P. W.; Stephenson, G. R.; Taylor, S. C. *J. Organomet. Chem.* **1989**, 370, 97. (c) Howard, P. W.; Stephenson, G. R.; Taylor, S. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1603.

⁵ Pearson, A. J.; Gelormini, A. M.; Pinkerton, A. A. *Organometallics*, **1992**, 11, 936.

⁶ (a) Hudlicky, T.; Reed, J. W. *Synlett* **2009**, 685. (b) Johnson, R. A. *Org. React.* **2004**, 63, 117. (c) Hudlicky, T.; Gonzales, D.; Gibson, D. T. *Aldrichimica Acta* **1999**, 32, 35. (d) Boyd, D. R.; Sheldrake, G. N. *Nat. Prod. Rep.* **1998**, 15, 309.

⁷ Reiner, A. M.; Hegeman, G. D. *Biochem.* **1971**, 10, 2530.

⁸ (a) Charest, M. G.; Lerner, C. D.; Brubaker, J. D.; Siegel, D. R.; Myers, A. G. *Science* **2005**, 308, 395. (b) Charest, M. G.; Siegel, D. R.; Myers, A. G. *J. Am. Chem. Soc.* **2005**, 127, 8292. (c) Myers, A. G.; Siegel, D. R.; Buzard, D. J.; Charest, M. G. *Org. Lett.* **2001**, 3, 2923.

⁹ For examples see: (a) Pearson, A. J.; Sun, H.; Wang, X. *J. Org. Chem.* **2007**, 72, 2547. (b) Pearson, A. J.; Sun, H. *J. Org. Chem.* **2007**, 72, 7693. (c) Han, J. L.; Ong, C. W. *Tetrahedron* **2005**, 61, 1501. (d) Knölker, H.-J.; Baum, E.; Kosub, M. *Synlett* **2004**, 1769.

¹⁰ For discussions of this nomenclature as applied to tricarbonyliron complexes, see: (a) Stephenson, G. R. Polyfunctional electrophilic multihapto-organometallics for organic synthesis. In *Handbook of Functionalised Organometallics*; Knochel, P., Ed.; Wiley-VCH: Weinheim, Germany, 2005; pp 569–626. (b) Stephenson, G. R.; Astley, S. T.; Palotai, I. M.; Howard, P. W.; Owen, D. A.; Williams, S. Regiocontrolled applications of transition metal π -complexes. In *Organic Synthesis Via Organometallics*; Dötz, K. H.; Hoffmann, R. W., Eds.; Vieweg: Braunschweig, Germany, 1991; pp 169–185. For recent examples, see: (c) Roe, C.; Stephenson, G. R. *Org. Lett.* **2008**, 10, 189. (d) Anson, C. E.; Malkov, A. V.; Roe, C.; Sandoe, E. J.; Stephenson, G. R. *Eur. J. Org. Chem.* **2008**, 196. (e) Roe, C.; Sandoe, E. J.; Stephenson, G. R.; Anson, C. E. *Tetrahedron Lett.*, **2008**, 49, 650. (f) Owen, D. A.; Malkov, A. V.; Palotai, I. M.; Roe, C.; Sandoe, E. J.; Stephenson, G. R. *Chem. Eur. J.* **2007**, 13, 4293.

¹¹ (a) Zhang, R.; Fan, W.; Twamley, B.; Berg, D. J.; Mitchell, R. H. *Organometallics* **2007**, 26, 1888. (b) Arce, M.-J.; Viado, A. L.; Khan, S. I.; Rubin, Y. *Organometallics* **1996**, 15, 4340. (c) Sato, Y.; Mori, M.; Shibasaki, M. *Tetrahedron: Asymmetry* **1995**, 6, 757. (d) Bandara, B. M. R.; Birch, A. J.; Chauncy, B. *J. Organomet. Chem.* **1993**, 444, 137. (e) Maier, G.; Wiegand, N. H.; Baum, S.; Wüllner, R.; Mayer, W.; Boese, R. *Chem. Ber.* **1989**, 122, 767. (f) Ashkenazi, P.; Kapon, M.; Ginsburg, D. *Tetrahedron* **1988**, 44, 6871. (g) Jendralla, H.; Jelich, K.; DeLucca, G.; Paquette, L. A. *J. Am. Chem. Soc.* **1986**, 108, 3731. (h) Foster, S. J.; Rees, C. W. *J. Chem. Soc. Perkin Trans. 1* **1985**, 719. (i) Paquette, L. A.; Daniels, R. G.; Gleiter, R. *Organometallics* **1984**, 3, 560. (j) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1976**, 98, 63. (k) Amith, C.; Ginsburg, D. *Tetrahedron* **1974**, 30, 3415.

¹² (a) Murakami, N.; Sugimoto, M.; Morita, M.; Kobayashi, M. *Chem. Eur. J.* **2001**, 7, 2663. (b) Knölker, H.-J.; Baum, E.; Gonser, P.; Rohde, G.; Röttele, H. *Organometallics* **1998**, 17, 3916. (c) Schönecker, B.; Hauschild, U.; Marquardt, V.; Günter, A.; Walther, D. *Z. Chem.* **1989**, 29, 218. (d) Li, L.; Perrier, R. E.; Eaton, D. R.; McGlinchey, M. J. *Can. J. Chem.* **1989**, 67, 1868. (e) Edwards, O. E.; Kolt, R. J. *Can. J. Chem.* **1987**, 65, 595. (f) Barton, D. H. R.; Gunatilaka, A. A. L.; Nakanishi, T.; Patin, H.; Widdowson, D. A.; Worth, B. R. *J. Chem. Soc. Perkin Trans. 1* **1976**, 821. (g) Evans, G.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1975**, 102, 507.

-
- ¹³ (a) Bandara, B. M. R.; Birch, A. J.; Raverty, W. D. *J. Chem. Soc. Perkin Trans. I* **1982**, 1755. (b) Whitesides, T. H.; Slaven, R. W.; Calabrese, J. C. *Inorg. Chem.* **1974**, *13*, 1895. (c) Birch, A. J.; Williamson, D. H. *J. Chem. Soc. Perkin Trans. I* **1973**, 1892.
- ¹⁴ Ashworth, R. W.; Berchtold, G. A. *J. Am. Chem. Soc.* **1977**, *99*, 5200.
- ¹⁵ Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc. Perkin Trans. I* **1973**, 1882.
- ¹⁶ Swern oxidation and use of Dess–Martin Periodinane were unsuccessful. There exists a sole report in the literature of the successful use of a chromium(VI) reagent to effect oxidation in the context of tricarboyliron(diene) alcohols: Birch, A. J.; Kelly, L. F.; Weerasuria, D. V. *J. Org. Chem.* **1988**, *53*, 278. We thus employed chromium trioxide as oxidant, obtaining **11** in only 9% yield; use of pyridinium chlorochromate afforded a marginal improvement (12%). Parikh–Doering oxidation was similarly low-yielding (7%).
- ¹⁷ Williams, M. J.; Deak, H. L.; Snapper, M. L. *J. Am. Chem. Soc.* **2007**, *129*, 486.
- ¹⁸ (a) Marchand, N. J.; Grée, D. M.; Martelli, J. T.; Grée, R. L.; Toupet, L. J. *J. Org. Chem.* **1996**, *61*, 5063. (b) Tao, C.; Donaldson, W. A. *J. Org. Chem.* **1993**, *58*, 2134.
- ¹⁹ (a) Knölker, H.-J.; Fröhner, W.; Reddy, K. R. *Eur. J. Org. Chem.* **2003**, 740. (b) Knölker, H.-J.; Fröhner, W. *Tetrahedron Lett.* **1997**, *38*, 4051. (c) Knölker, H.-J.; Schlechtingen, G. *J. Chem. Soc. Perkin Trans. I* **1997**, 349. (d) Knölker, H.-J.; Budei, F.; Pannek J.-B.; Schlechtingen, G. *Synlett* **1996**, 587. (e) Knölker, H.-J.; Bauermeister, M. *Helv. Chim. Acta.* **1993**, *76*, 2500. (f) Knölker, H.-J.; Bauermeister, M. *Tetrahedron* **1993**, *49*, 11221. (g) Knölker, H.-J.; Bauermeister, M.; Pannek, J.-B.; Bläser, D.; Boese, R. *Tetrahedron* **1993**, *49*, 841. (h) Knölker, H.-J.; Bauermeister, M. *Heterocycles* **1991**, *32*, 2443. (i) Knölker, H.-J.; Bauermeister, M. *J. Chem. Soc., Chem. Commun.* **1990**, 664. (j) Knölker, H.-J.; Bauermeister, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1468. (k) Knölker, H.-J.; Bauermeister, M.; Bläser, D.; Boese, R.; Pannek, J.-B. *Angew. Chem.* **1989**, *101*, 225. (l) Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A.; Wild, S. B. *J. Chem. Soc. A* **1968**, 332.
- ²⁰ Birch, A. J.; Chamberlain, K. B.; Thompson, D. J. *J. Chem. Soc. Perkin Trans. I* **1973**, 1900.
- ²¹ Watanabe, A.; Kamahori, T.; Aso, M.; Suemune, H. *J. Chem. Soc. Perkin Trans. I* **2002**, 2539.
- ²² The corresponding protons in the complex lacking the ester (**2**, R=H) have not been assigned unambiguously.
- ²³ Kruczynski, L.; Takats, J. *Inorg. Chem.* **1976**, *15*, 3140.
- ²⁴ (a) Sheldrick G. M. *Acta. Cryst.* **1990**, *A46*, 467. (b) Sheldrick, G. M, *SHELXL-97*, a computer program for crystal structure refinement, University of Göttingen, **1997**.